A question of time: Royal Society Medallist's Lecture for 1993

J R De Laeter

Department of Applied Physics, Curtin University of Technology,
Perth, Western Australia, 6001

Manuscript received November 1993

The cheeseboard is the world, the pieces are the phenomena of the universe, the rules of the game are what we call the laws of nature. The player on the other side is hidden from us. We know that his play is always fair, just, and patient. But also we know, to our cost, that he never overlooks a mistake, or makes the smallest allowance for ignorance.

T H Huxley, 1868
A Liberal Education

Introduction

I am honoured that the Royal Society of Western Australia has conferred on me the Royal Society Medal for 1993. As a member and Past President of the Society, I am pleased that my colleagues have seen fit to recognise my research, which has almost in its entirety been carried out in Western Australia, first at the University of Western Australia, then at the Western Australian Institute of Technology and subsequently at Curtin University. I dedicate this lecture to my wife and family and research colleagues who have made this award possible. I would also like to thank His Excellency, the Governor of Western Australia, Major General Michael Jeffrey, for presenting the Royal Society medal to me on the occassion of this lecture.

I have chosen **"A Question of Time"** as my topic for this Medallist's address, and I would like to explore with you some of the questions which all of us have asked:-

How old is the Universe?
How long did the Sun take to form?
How old is the Solar System?
How old is this rock?

The concept of time has never ceased to intrigue and puzzle those who think about it. We instinctively feel that time goes on unceasingly, and that there is nothing we can do to halt its inexorable progress. However, Albert Einstein has taught us that time is not immutable; rather it is relative and depends on the observer. I wish to consider time as the order in which events occur. How then are we to measure geological time?

For centuries various people tried to estimate the age of the Earth by heat flow (Lord Kelvin), by tidal interaction (George Darwin), by the saltiness of the oceans (Edmond Halley) and by the accumulation of sediments (Charles Walcott). However, none of these "clocks" was particularly accurate, and the physicist Lord Kelvin fell into disrepute with geologists because his estimated age of 10 million years, which he obtained by examining the cooling of the Earth from a molten body, was far too short as far as the geologists were concerned.

Then in 1896 came the breakthrough that was needed to measure geological time. Henri Becquerel discovered that certain minerals were radioactive, and Marie and Pierre Curie then showed that these radioactive atoms change into other atoms at regular and constant rates. After a certain period of time, exactly half the radioactive parent atoms decay to daughter atoms - this period is the half-life of the radioactive parent. Provided one knows the value of the half-life and the proportion of parent to daughter atoms, we can calculate the period of time over which the parent has been decaying, subject to the fact that the system has been "closed" over the time interval concerned.

In 1902 two scientists at McGill University in Canada, the New Zealand physicist Ernest Rutherford and the English chemist Frederick Soddy, investigated the radioactive decay of uranium and showed that it decayed to a daughter product (lead) and also produced helium from the alpha particles emitted. In 1905 in the Silliman lectures at Yale, Rutherford suggested the possibility of using radioactivity as a geological timekeeper, on the basis that if one could measure either of the daughter products helium or lead, then one could measure geological time by this uranium nuclear clock (Rutherford, 1906).

Unfortunately the only means available at that time to measure helium and lead were chemical techniques, and both suffered from serious shortcomings. Helium, being a gas, leaked out of uranium-rich ores, especially if they were weathered, and thus the calculated ages were very much minimum estimates. The measurement of the quantity of lead could not distinguish the daughter-product lead from primordial lead, and so calculated ages were overestimated.

In the early part of this century, before the establishment of the University of Western Australia, Perth Technical College offered undergraduate degrees in science, in collaboration with the University of Adelaide. In 1904 a group of Western Australians, in an endeavour to gain support for a University, persuaded Frederick Soddy who by then was based in England, to make the long sea-voyage to Australia during his University vacation to give a series of lectures in Perth, Fremantle and Kalgoorlie on the latest scientific results. One of Soddy's lectures concerned radioactivity and the determination of the age of the Earth.

© Royal Society of Western Australia 1994

He argued that Kelvin's estimate of the age of the Earth was "absolutely wrong", and postulated that the Earth was heated by the energy released by radioactive decay (Jenkin 1985).

E S Simpson, who in 1904 was Chemist and Assayer of the Geological Survey of WA, took a keen interest in Soddy's lectures. Simpson later became the President of the Royal Society of WA and was awarded the Royal Society Medal in 1929. In 1910 Simpson received samples of a bright-yellow uranium mineral from a pegmatite at Wodgina in the Pilbara. He named it "Pilbarite", measured the amount of helium in it, and calculated its age to be 13 Ma although he pointed out that this age was of no significance due to helium leakage (Simpson 1910). He also chemically analysed two other minerals from the same pegmatite which he identified as mackintoshite and thorogummite. Although Simpson measured the amount of lead in these minerals, he did not publish their ages and it was not until 15 years later that Professor L A Cotton, a geologist at the University of Sydney, used Simpson's analytical data to calculate the uranium-lead ages of these three minerals (Cotton 1926). These published ages were 1475, 1460 and 3840 Ma for the mackintoshite, thorogummite and pilbarite specimens respectively. Holmes & Lawson (1927) revised Cotton's calculations, and an age of 1260 Ma for the mackinstoshite sample was included in a popular book in the same year (Holmes 1927). This was the oldest age recorded in Holmes' book, and so the widespread belief arose that Western Australia possessed the Earth's oldest material.

It is amazing to think that in 1910, a few years after the discovery of the uranium nuclear clock by Rutherford, that a Western Australian scientist should have measured the age of a Pilbara mineral. However, Simpson did not maintain his interest in age determinations, and in a letter in 1927 politely rejected a suggestion from Sir Douglas Mawson, the Antarctic geologist, that he should continue such work.

Mass spectrometry and the modern era of geochronology

The chemical method of determining uranium-lead ages was fraught with many errors, and little progress was made in refining such ages until the discovery of isotopes by J J Thomson at the Cavendish Laboratory at Cambridge in 1912. F W Aston, using a vastly improved mass spectrometer, was able to show that lead had at least three isotopes. In 1929, he showed that a uranium-rich sample of broggerite was highly enriched in ^{206}Pb, and calculate on age of ^{909}Ma (Aston 1929). This heralded a new era in geochronology, based on physical rather than chemical methods. Since that time, the mass spectrometer has become the tool of every practising geochronologist - a veritable time machine which enables us to explore the past. An even more significant conclusion from Aston's isotopic results was drawn by Rutherford, who calculated the age of the Earth to be 3.4 x 109y (Rutherford 1929). This marked the advent of cosmochronology.

In 1940, Alfred O Nier of the University of Minnesota designed a simple mass spectrometer which could measure the isotope abundances of elements with good accuracy (Nier, 1940). His sector field mass spectrometers are now common in geochronological laboratories around the World. He has rightly been called the "father of modern mass spectrometry". Nier was able to calculate a U-Pb age of 2570±70 Ma for a monazite (Nier *et al.* 1941), and later pioneered the K-Ar geochronological technique (Aldrich & Nier 1948).

A mass spectrometer measures the relative abundances of the isotopes of an element by separating the various masses in a transverse magnetic field (Fig 1). The sample is mounted on a filament in the ion source of the mass spectrometer. Thermal energy ionises the atoms, and the resulting positive ions are accelerated from the source into the magnet, and subsequently the dispersed ions are collected in a detector. Varying the magnetic field enables ions of different mass to be brought to a focus in the detector, and hence the relative isotopic abundances of the element in the particular sample can be measured.

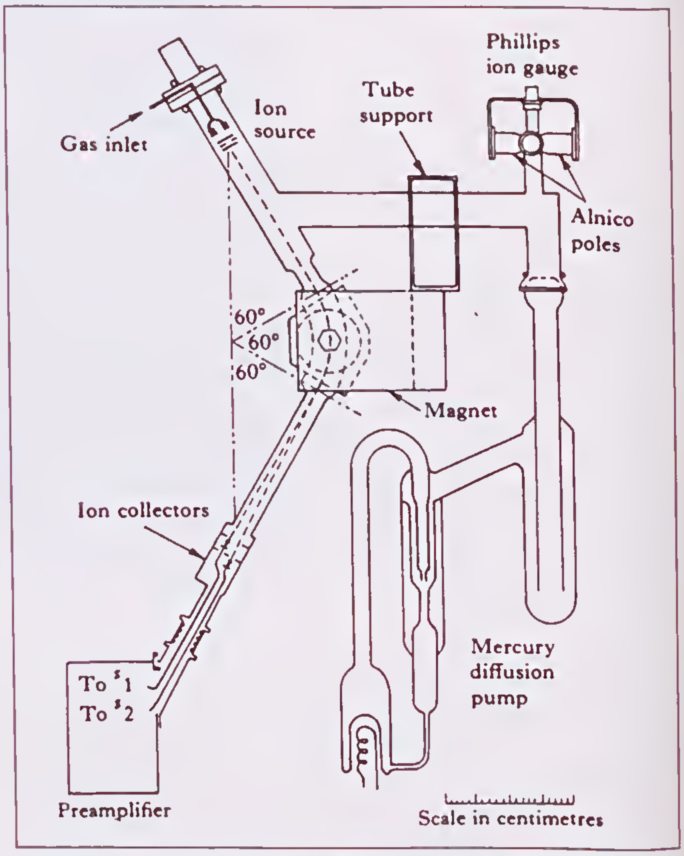

Figure 1. Schematic diagram of a Nier 60 magnetic sector mass spectrometer showing the ion source, magnet and collector assembly.

The Physics Department at the University of Western Australia

In the late 1940's two young physics lecturers at the University of Western Australia (UWA) - Peter Jeffery and Hilary Morton - were building a small nuclear accelerator. On his way to take up a foundation position at the Australian National University (ANU), Sir Marcus Oliphant visited the Physics Department and suggested to Jeffery and Morton that they should build a mass spectrometer and initiate a geochronological research program. Oliphant was a student of Rutherford and was familiar with the physical technique used in geochronology. He referred to the widespread belief that Western Australia contained the Earth's oldest minerals, and that geochronology would be a good field of research for the University to undertake.

Jeffery and Morton built a mass spectrometer out of copper tubing and other odds and ends, but by 1953 had decided to abandon the project unless financial support could be found. Morton in fact left Perth to go to ANU, but Jeffery persevered with a grant from the Carnegie Geophysical Institute in Washington, DC. Jeffery (1976) describes the effect of these funds in the following terms:

> "The Carnegie funds provided the Perth group with a new sixty degree Nier-type mass spectrometer and also permitted the original home-made spectrometer to be upgraded by the replacement of its waterpipe sections with fabricated stainless steel. Such exotic devices as a chart recorder to replace a wall galvanometer, and commercial diffusion pumps were all very acceptable. In spite of these improvements in equipment however, ion currents were still being measured using 'acorn' 954s as electrometers"

I joined the mass spectrometry group at UWA in 1954 as an honours student in physics, and worked with Peter Jeffery and a PhD student - Bill Compston - on carbon isotopes using the "copper tube" mass spectrometer. I was fortunate to be a co-author of the first paper ever published by the mass spectrometry group which described this work (Jeffery *et al.* 1955). The second machine was commissioned by another PhD student, David Greenhalgh in 1955, and the first U-Pb age date was published in 1959 (Greenhalgh & Jeffery 1959).

Peter Jeffery spent 1955 at the Carnegie Institute in Washington DC, and on his return commenced a program of Rb-Sr dating. Bill Compston, who had subsequently completed a Postdoctoral Fellowship at the California Institute of Technology (Cal Tech), became a lecturer in Physics at UWA, and they were joined by a PhD student (Glen Riley) to develop the Rb-Sr technique - which is based on the decay of the radioactive parent ^{87}Rb to the stable daughter ^{87}Sr. The half life of ^{87}Rb is 4.88×10^{10}y, and this chronometer is therefore ideally suited for old rocks.

Towards the end of the 1950's, the validity of the Rb-Sr method was being questioned since mineral separates from whole rock samples gave different results. A granite from the Boya quarry was analysed to give ages of 2430 Ma for the whole rock specimen, 650 Ma for the biotite, and 1290 Ma for the microcline extracted from the sample. Compston & Jeffery (1959) argued that the mineral separates had lost a proportion of their radiogenic 87Sr some time after crystallisation, presumably through a metamorphic event, but that the 87Sr was not lost to the whole rock and was simply redistributed within it.

Dr Alan Wilson from the Geology Department at UWA joined forces with Jeffery, Compston, Greenhalgh and Riley to exploit these geochronological techniques in the southern Yilgarn Block and the Albany Fraser Province. A paper by the group in 1960 reported 36 Rb-Sr, 16 K-Ar and 21 U-Pb ages (Wilson *et al.* 1960). The collaboration of physicists and geologists represented an important advance, in that the combined talents of field geologists and laboratory physicists were available to tackle this new field of scientific research which was of enormous potential value to mineral exploration in this State.

After the success of the 1950s, one might have assumed that the University of Western Australia would have become one of the world's leading centres for geochronology, situated as it was in a mineral-rich State with extensive Precambrian terrains. This was not the case. By 1961, the geochronological program at UWA was non-existent. Bill Compston took up a position at ANU, Glen Riley went to the Australian Institute of Nuclear Science and Engineering, Alan Wilson moved to Queensland, David Greenhalgh became a science teacher, and Peter Jeffery developed new interests in nuclear astrophysics in cooperation with John Reynolds at the Physics Department in the University of California at Berkeley. When Dr Jeffery returned to Perth in 1962, I became his first PhD student in nuclear astrophysics.

Geochronology at the Western Australian Institute of Technology

On my appointment as Inaugural Head of the Department of Applied Physics at the Western Australian Institute of Technology (WAIT) in 1968, after a Post Doctoral fellowship at McMaster University in Canada, a research program to search for isotopic anomalies in meteorites was established using a 30cm radius of curvature solid source mass spectrometer. In late 1968, Dr Alec Trendall of the Geological Survey of Western Australia (GSWA) and Bill Compston argued that some mass spectrometer time should be devoted to geochronology, because of the necessity to place time constraints on the rock units being mapped by geologists at the GSWA, and the inability of Compston's ANU laboratory to handle the immense amount of work that needed to be done. The Rb-Sr technique was chosen because it was relatively simple and ideally suited to the old Archaean rocks which constituted a major portion of the State, and which was the focus of much of the geological mapping at that time. The first geochronological paper from the WAIT laboratory was published in 1970 (De Laeter & Trendall 1970).

In the early 1970s we decided to develop a new geochronological technique based on the decay of ^{176}Lu to ^{176}Hf, with a half life of 3.54×10^{10}y. Although the mass spectrometry of hafnium presents some difficulties, the Lu-Hf chronometer has some characteristics which made it an attractive research project. However, our interests were diverted from geochronology to cosmochronology and thus the Lu-Hf geochronometer was not developed at that time (McCulloch *et al.* 1976). Malcolm McCulloch later was instrumental in developing the Sm-Nd geochronological technique at Cal Tech (McCulloch & Wasserburg 1978a), before taking an appointment at ANU.

The Sm-Nd technique is based on the decay of ^{147}Sm to ^{143}Nd with a half life of 10.6×10^{10}y. As parent and daughter are both rare earth elements, natural fractionation processes do not favour a separation as occurs for many pairs of elements used in geochronology. This technique was introduced at WAIT in 1979 (Fletcher & Rosman 1980), and has been used successfully to solve a number of geochronological problems.

By the mid-1970s, geochronology was a major component of the work of the mass spectrometer laboratory at WAIT. In 1974 geologists from the University of Western Australia became associated with the mass spectrometry laboratory, and an extensive survey of Yilgarn ages was carried out using the Rb-Sr technique. With the appointment of Dr M T Bickle to the Geology Department of UWA in 1979, the tempo of the geochronology program accelerated, and a number of articles have subsequently been published on the Yilgarn Block (Chapman *et al.* 1981) and on the Pilbara Block (Bickle *et al.* 1983). A U-Pb chemical extraction laboratory was established at UWA, and the U-Pb and Pb-Pb geochronological techniques complemented the existing Rb-Sr and Sm-Nd techniques.

The appointment of Dr R T Pidgeon at WAIT in 1981 heralded the introduction of zircon geochronology as yet another geochronological technique available in Western Australia, and there was a corresponding increase in the scientific output of the geochronology group which now comprised geologists and physicists from GSWA, UWA and WAIT. Scientists from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and industry have also been associated with a number of research projects. A close liaison with geochronologists at ANU has also been a feature of our work. More recently Dr Neal McNaughton was appointed to UWA and he and his students have been actively associated with the laboratory. Together with Ian Fletcher and Kevin Rosman, Neal McNaughton has developed the K-Ca geochronological technique.

In 1979 the Royal Society commissioned a number of reviews describing aspects of science in Western Australia from 1829 to 1979 on the occasion of the 150th Anniversary of the founding of Western Australia. One of these concerned geochronology (De Laeter & Trendall 1979). Figure 2 shows the rate of growth in geochronologically - based publications from 1910 to 1977 taken from that paper.

For the Yilgarn Block

- the time of major generation of gneisses and granitoids was remarkably consistent over almost the entire sampled area of the block, and peaked at about 2700 my;
- there is little evidence for any wide spread about this peak, and evidence for much older ages is still not compelling;
- over a large area of the Block, the granitoids had a relatively short prior-crustal history, and by implication were generated over a relatively brief period;
- the time interval between the formation of the greenstone belts and the peak of granitoid emplacement is of unknown length, but the available evidence suggests that it was small.

For the Pilbara Block

- the main period of gneiss and granitoid generation was also uniform over the area of the Block, and was earlier than that in the Yilgarn Block;
- the error limits attached to granitoid ages make it uncertain whether emplacement was restricted within a narrow time range;
- the highly fractionated small-volume granitoids ("tin granites") are significantly younger;
- greenstone belt ages are about 300-500 Ma older than the peak granitoid age.

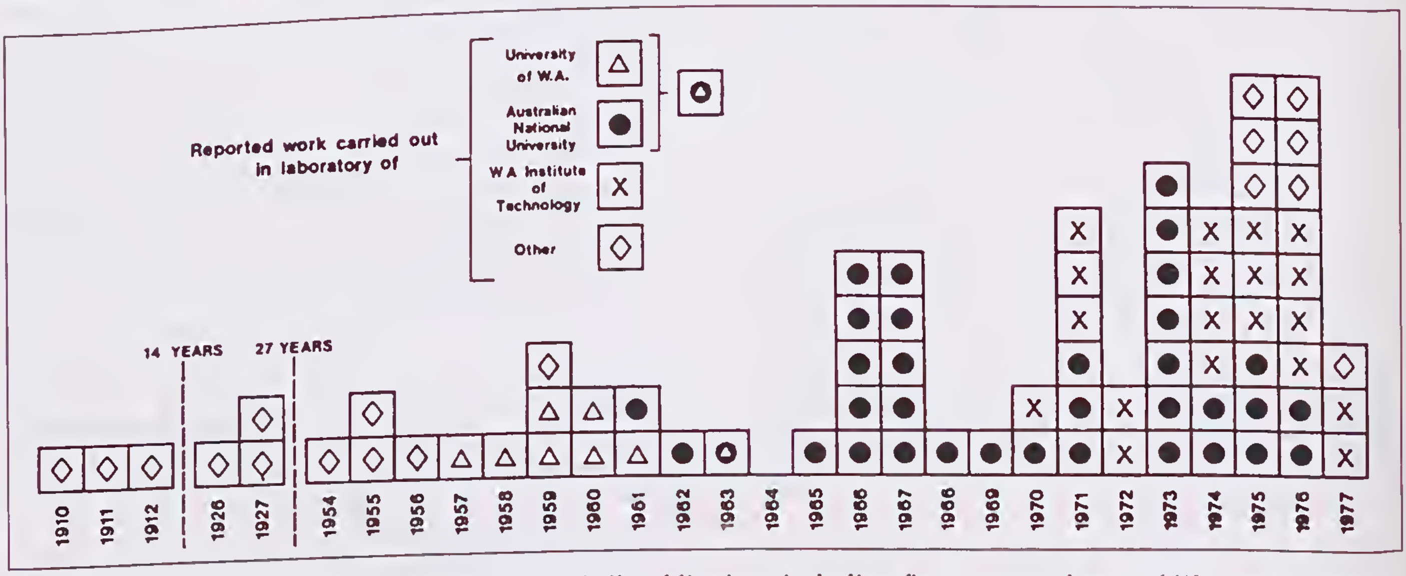

Figure 2. Chronological summary up to 1977 of all publications including first reports of ages of Western Australian Precambrian rocks and minerals by methods based on radioactive decay. Selected second reports are also included where these augment or upgrade the first.

In 1981, on the occasion of the 2nd Archaean Conference in Perth, a review of the geochronological data on the two major Archaean terrains of Western Australia was published (De Laeter *et al.* 1981). At that time most of the dates were from Rb-Sr analyses (837 whole-rock and 142 mineral Rb-Sr ages), 137 mineral Pb isotope analyses, and 15 K-Ar analyses, together with some U/Pb data. The judgement was made that, despite the large database, disappointingly few firm conclusions could be enunciated. Nevertheless, the following conclusions were drawn from these data (De Laeter *et al.* 1981):

Zircons are Forever

One of the most intriguing episodes in Western Australian geochronology has been the search for the oldest rocks. In 1981, Denis Gee and his colleagues at the GSWA argued that a predominantly gneissic terrain, which forms an area around the western margin of the Yilgarn Block, was of great antiquity (Gee *et al.* 1981). A study of banded gneisses near Mt Narryer in the northern part of the Western Gneiss Terrain gave a Rb-Sr whole rock isochron age of 3348±43 Ma with an initial $^{87}Sr/^{86}Sr$ ratio of 0.7037 (De Laeter *et al.* 1981). A prior crustal history of approximately 200 Ma could be inferred, and this was supported by Sm-Nd model ages of 3620 Ma to 3710 Ma from samples of this Meeberrie gneiss (Fig 3). Further work gave a Pb-Pb isochron of 3357 ±70 Ma, whereas Rb-Sr ages for granites intruding the gneisses gave the classic Yilgarn age of approximately 2600 Ma (De Laeter *et al.* 1985). The Sm-Nd ages were interpreted as the time of extraction of the protoliths of the gneisses from a chrondritic source, whilst the Rb-Sr age is thought to represent a time of intracrustal reworking of the gneisses.

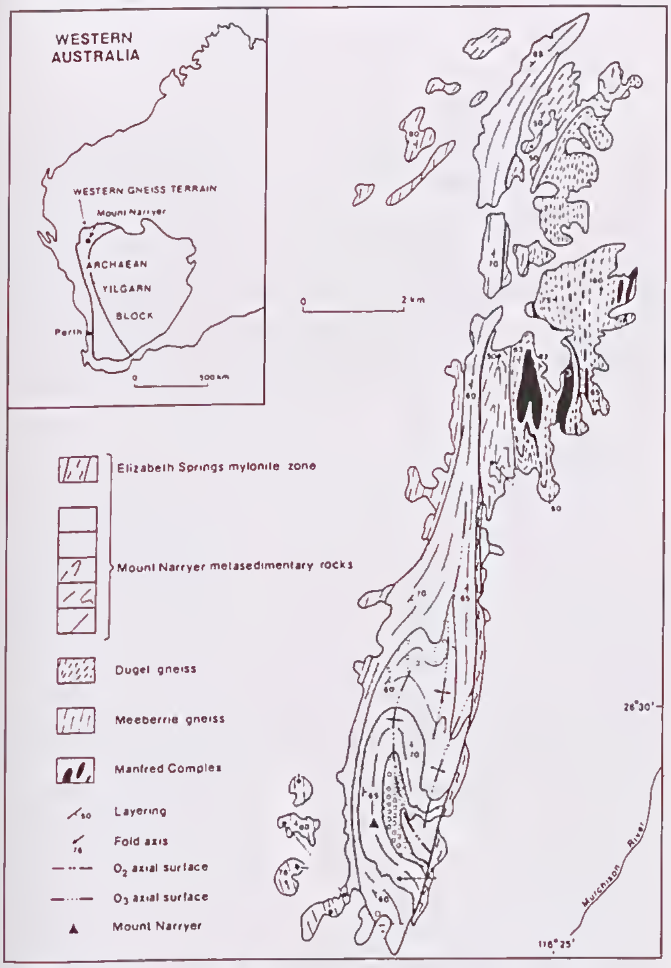

Figure 3. Simplified geological map of the Mt Narryer region, Western Australia.

It was about this time that the Sensitive High Resolution Ion Micro Probe mass spectrometer (SHRIMP) in the Research School of Earth Sciences at ANU became available for zircon geochronology. Designed by Steve Clement, SHRIMP was the "brainchild" of Bill Compston. After years of development it had already produced some exciting results using the zircon method. However, there was a certain amount of scepticism in various parts of the world as to its real capabilities. Zircons from one of the Meeberrie gneiss samples gave a U-Pb age of 3300 Ma for the rims of the zircons whilst the interior portions gave ages between 3560-3690 Ma (Kinny *et al.* 1988). These older ages have been interpreted as minimum estimates for the original magmatic ages of the xenocrystic cores. These data were in excellent agreement with the conventional geochronology carried out at WAIT, and were convincing evidence of the power of ion probe mass spectrometry.

U-Pb studies by the ion microprobe on detrital zircons from quartzite adjacent to the banded gneiss showed that most of them formed between 3500 and 3750 Ma, although some of them gave ages of about 3300 Ma (Froude *et al.* 1983). These ages suggest that the zircons may have been derived by erosion of the adjacent gneisses or their protoliths. In addition Froude *et al.* (1983) reported the existence of four zircons from the same quartzite which have nearly concordant U-Pb ages between 4100 and 4200 Ma. These results suggest that pre-3800 Ma silica-saturated rocks were present in the Earth's crust. It is possible that intact remnants of these rocks may have survived in this region.

The Jack Hills metasedimentary Belt is a narrow curvilinear east to north-east trending belt approximately 60 km north-east of Mount Narryer. It is composed of minor metabasalts and substantial thicknesses of chert and banded iron formation interleaved with pelitic and psammitic metasediments (Compston & Pidgeon 1986). Detrital zircons from the Jack Hills metasedimentary belt analysed at ANU using the ion microprobe mass spectrometer, has revealed the oldest ages so far determined. One zircon grain registers an age of 4276±6 Ma. which is a minimum estimate for its original age (Compston & Pidgeon 1986). Sixteen other grains have the same or slightly younger age, similar to the zircon ages measured at Mount Narryer. The frequency of occurrence of the old zircons is 12±5%.

Kober *et al.* (1989) report the analyses of thirty zircon crystals from the Jack Hills metaconglomerate using the single zircon, direct evaporation, thermal ionization technique. Four of the thirty zircons gave ages in excess of 4000 Ma, confirming the microprobe analyses of Compston & Pidgeon (1986). Approximately 50% of the analysed zircons yielded an age of 3380±20 Ma, whilst other crystals gave ages of 3300 Ma, 3440 Ma and 3570 Ma. As had been observed at Mount Narryer, some of the zircons demonstrated a more complex age structure with intergrowth of the old phases with younger domains.

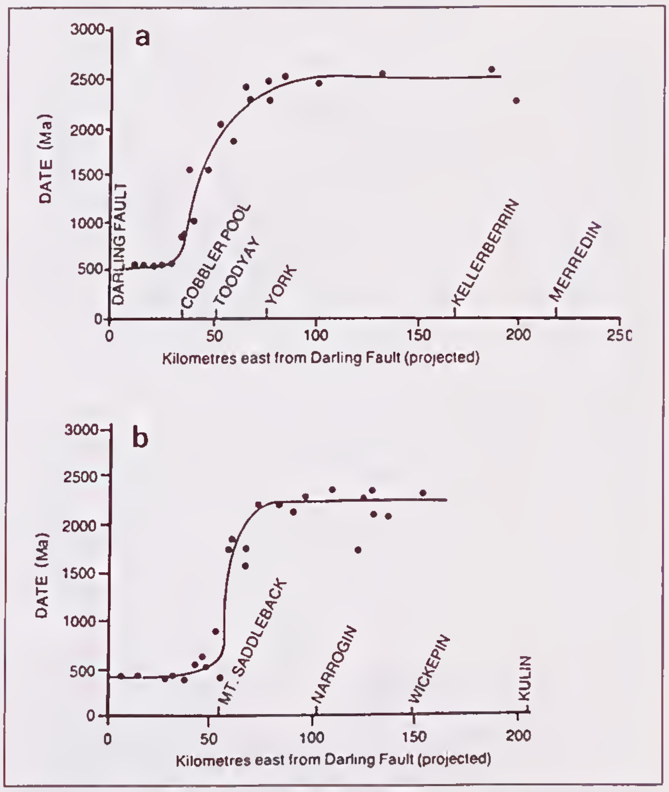

Figure 4. Time-space plots of (a) the Perth and (b) Harvey traverses. Localities have been projected parallel to the western edge of the transition zone, the traverse line being normal to the transition zone.

Although parent rocks with ages in excess of 4000 Ma have not been found, the long-standing belief that Western Australia possesses the Earth's oldest material has been vindicated.

The most recent geochronological publication from the mass spectrometry laboratory at Curtin was in the last issue of the Australian Journal of Earth Sciences (De Laeter & Libby 1993). It describes a profile of Rb-Sr biotite ages from Perth to Kellerberrin and from Harvey to Kulin (Fig 4). The Rb-Sr system for biotites can be reset if the temperature of the rocks exceeds approximately 320C. The ages are between 430-500 Ma in the western most area, then climb quickly through a transition zone, and then are roughly constant at 2300 Ma to the east. We interpret these profiles as representing a period of uplift in the early Palaeozoic.

Cosmochronology

One of the most challenging tasks in nuclear astrophysics is to place a time scale on the events that have occurred in the nucleosynthesis of the chemical elements and on the formation and evolution of the Solar System. Although this is a daunting task, we are aided in our search by the occurrence of a large number of radionuclides, with a wide array of half-lives, that provide the variety of nuclear clocks necessary to achieve this objective. To obtain accurate dating, a decay system should be selected with a half-life that is of the same order as the age of the material to be measured. Thus, long-lived radioactive decay schemes such as U-, Th-Pb, Sm-Nd, Rb-Sr, K-Ar, Re-Os, Lu-Hf and K-Ca have been used to measure the age of events that occurred early in the history of the Solar System, whereas short-lived radionuclides such as ^{10}Be, ^{36}Cl, ^{14}C, ^{3}H, and the U-series disequilibrium system have been used to study more recent events.

Geochronology utilizes isotopic dating techniques to measure the age of terrestrial materials. The radioactivity of certain nuclides also enables them to be used as isotopic tracers of geological processes, such as differentiation sequences in igneous rocks and in the study of mantle-crustal relationships. Isotope geology has now reached a high degree of sophistication, which has only been made possible by the development of sensitive mass spectrometers that are capable of routine measurements of high precision and accuracy. Conventional gas source and solid source mass spectrometers have been successfully applied to the long-lived chronometers, but the short-lived chronometers have required instrumentation with the best possible sensitivity. Ion probe and accelerator mass spectrometers are two such recent developments. Unfortunately the dating of terrestrial materials does not provide a great deal of information on the time of formation of the Solar System, since the Earth is an active planet where a variety of geological processes have combined to destroy the early record of its history.

There are three major epochs in the history of the cosmos. The first epoch *T* extends from the "Big Bang" to that time when the solar nebula was isolated from galactic nucleosynthesis. The second epoch Δ is of relatively short duration and represents the time interval for the collapse of a gas cloud leading to the formation of the Solar System. The third epoch T_{ss} represents that period from the formation of the Solar System to the present (Figure 5).

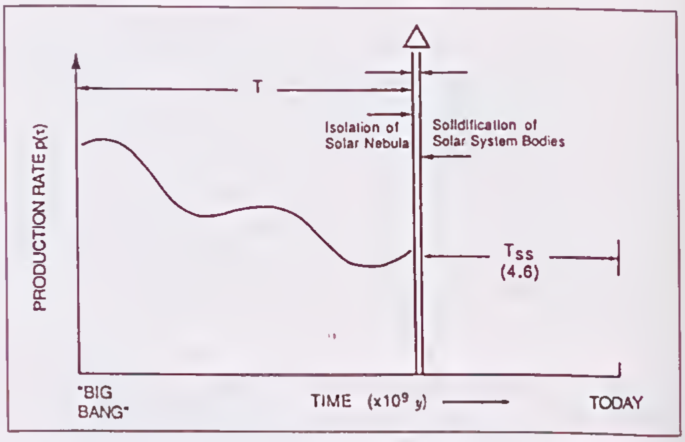

Figure 5. A schematic diagram of the history of the Universe. The first epoch *T* represents the time period from the "Big Bang" to the isolation of the solar nebula from galactic nucleosynthesis. The second epoch Δ is the time interval between the termination of nucleosynthesis and the solidification of Solar System bodies, while the third epoch T_{ss} represents the age of the Solar System. The shape of the production rate for nucleosynthesis, $p(\tau)$, is for illustrative purposes only.

The Age of the Solar System

Meteorites and lunar samples provide us with alternative avenues to determine the age of the Solar System T_{ss}. Meteorites are the debris of small planetary bodies that solidified early in the history of the Solar System and have been closed isotopic systems retaining evidence of early Solar System processes. Neither have they been subjected to the long planetary accretion processes associated with larger bodies. The first isotopic determination of the age of the Solar System was carried out in 1953 on primordial meteoritic lead (Patterson 1956), resulting in an age of formation for planetary bodies of ~4.5 x 10^9 years. Exacting chronological studies of a variety of meteoritic materials show that a fine-scale separation of events took place early in the Solar System during planetary formation, and these events may be resolved down to a few million years (Wasserburg 1987).

Numerous chronological investigations of lunar materials were carried out on samples obtained during the various missions to the Moon, from which an excellent chronology has been determined (Wasserburg *et al.* 1977). Figure 6 shows a representation of lunar chronology. Crystallisation ages of approximately 4.5 x 10^9 years have been obtained from lunar rocks, so that there is a good correspondence between the meteoritic and lunar data for the time of planetary formation. The melt rocks derived from impact metamorphism give crystallisation ages of (3.85-4.05) x 10^9 years, and there is good agreement between the U, Th-Pb, Rb-Sr and K-Ar data. This is interpreted as the result of a major bombardment of the moon by meteorites which created the lunar basins. This has been called the "terminal lunar cataclysm", and it is possible that this bombardment affected the Solar System as a whole (Tera *et al.* 1974). After the termination of the bombardment phase some 3.85 x 10^9 years ago, there was continued but decreasing volcanic activity until approximately 3.0 x 10^9 y ago, after which the lunar surface appears quiescent. There is no evidence of recent igneous activity on the moon.

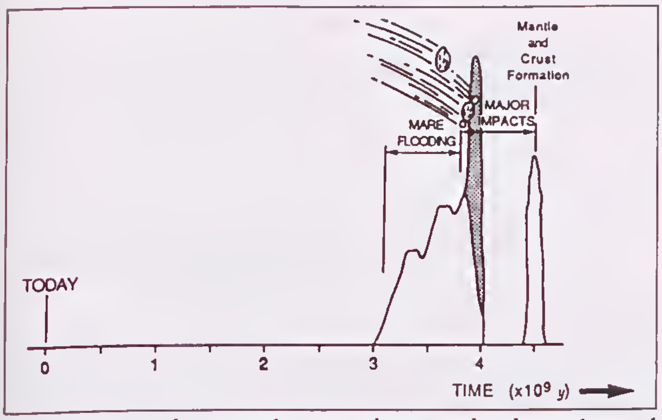

Figure 6. A schematic diagram showing the chronology of major lunar events.

My involvement with the chronology of lunar samples was quite peripheral. In 1971 a fire in a chemical preparation room adjacent to the mass spectrometer laboratory at WAIT badly damaged the mass spectrometer which had been installed in 1968. Although the cost of replacement was covered by insurance, there was a time lag before a new machine could be installed. Fortuitously, Bill Compston was taking up a six month appointment at the Lunar Science Institute in Houston, Texas, and he asked me to supervise his laboratory at ANU during his absence. It was the time of the Apollo missions, and geochronologists were trying to measure the ages of the returned lunar samples. There was intense competition to determine the ages by a variety of techniques, and national as well as personal prestige was at stake.

Bill Compston's ANU laboratory had reported Apollo 14 Rb-Sr ages which were systematically greater by a few percent than other reported measurements. Compston was to present a paper at the Lunar Conference which would attempt to justify the ANU results. However, there was a possibility that the elemental Rb/Sr ratios measured at ANU on the lunar samples were wrong, because of systematic errors in the calibrations of the Rb and Sr isotopic spikes. The US National Bureau of Standards had just produced some certified stoichiometric Rb Cl (SRM 984) and Sr CO_3 (SRM 987) standards and it was decided to recalibrate the ANU spike solutions against these new standards. Working around the clock, we managed to complete the work just before the Lunar Science lecture where Bill Compston was able to announce a 1.8% error in the calibrations which necessitated a decrease in all the previous ANU ages for the Apollo samples. The revised ages were then in good agreement with Wasserburg's group at Cal Tech (De Laeter *et al.* 1973). I also worked on the Apollo 15 lunar samples at ANU before returning to Perth in mid 1972 (Compston *et al.* 1972).

Extinct Radionuclides

A number of unsuccessful mass spectrometric attempts were made to demonstrate the existence of short-lived radionuclides early in the evolution of the Solar System before John Reynolds showed that a large enrichment of ^{129}Xe existed in Xe extracted from the Richardton meteorite (Reynolds 1960). In 1961 Peter Jeffery and Reynolds proved that the excess ^{129}Xe was correlated with iodine in the meteorite, thus proving that the decay of the radionuclide ^{129}I (whose half-life is 17 x 10^6), had taken place within the meteorite itself (Jeffery & Reynolds 1961). It was possible to calculate a time Δ~10^8 years between the synthesis of ^{129}I and the formation of the Solar System. The value of Δ~10^8 years created somewhat of a dilemma, because astrophysical models predicted a much shorter time interval for the formation of the Solar System.

One reason behind the search for evidence of extinct radionuclides in meteorites was to identify the heat source that melted some of the meteorite parent bodies. One of the most logical candidates was ^{26}Al, which decays to ^{26}Mg with a half-life of 0.72 x 10^6 years. I was associated with the first mass spectrometric study to identify the presence of this potential heat source by the measurement of the isotopic composition of Mg in meteoritic feldspars whilst I was at McMaster University in 1967 (Clarke *et al.* 1970). Although this initial attempt was unsuccessful, a study of calcium-aluminium rich inclusions from the Allende meteorite by Chris Gray and Bill Compston gave an excess in ^{26}Mg, which was shown to be correlated with Al, in an isochron-type array (Gray & Compston 1974). Figure 7 shows an ^{26}Al/^{26}Mg isochron from Lee *et al.* (1977). A plausible interpretation is that ^{26}Al was present in the meteorite and that the decay was *in-situ*. If it is assumed that the minerals were isotopically homogeneous at the time of solidification, a value of Δ of ~ 10^6 years can be calculated. This is significantly lower than the value of ~10^8 years derived from ^{129}I-^{129}Xe systematics, and much closer to astrophysical estimates.

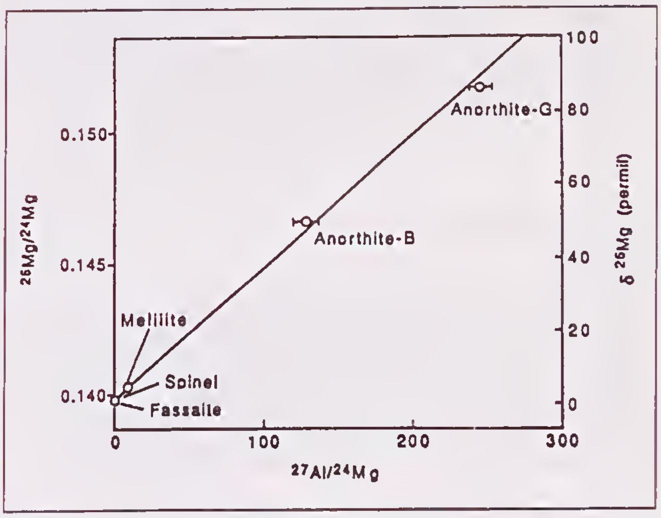

Figure 7. An "isochron" diagram of ^{26}Mg/^{24}Mg versus ^{27}Al/^{24}Mg for minerals from an Allende inclusion. The linear dependence of the magnitude of the anomalous ^{26}Mg on the Al/Mg ratio can be interpreted as resulting from the decay of the radioactive nuclide ^{26}Al.

Another extinct radioactive system is based on the decay of ^{107}Pd (with a half-life of 6.5 x 10^6 a) to ^{107}Ag. Kelly & Wasserburg (1978) proved the existence of excess ^{107}Ag in iron meteorites with ^{107}Ag excesses of up to 20%. The excess ^{107}Ag correlates with Pd to form an "isochron" with a calculated Δ of ~ 10^7 years between the last injection of nucleosynthetic material and the melting and differentiation of small planetary bodies. A ^{135}Ba enrichment, which was observed in an Allende inclusion by McCulloch & Wasserburg (1978b), is due to the decay of ^{135}Cs (which has a half-life of 3.3 x 10^6).

A number of other extinct radionuclides may be present in meteoritic material. Kevin Rosman and I investigated the decay of ^{126}Sn to ^{126}Te (with a half life of 10^5) in iron meteorites, but could find no evidence of excess ^{126}Te. This provides a lower limit of 10^6 years for Δ (De Laeter & Rosman 1984).

The study of extinct radionuclides therefore provides the following scenario: interstellar material, containing a full range of nucleosynthetic products (including some radionuclides that are now extinct), condensed to form a molecular cloud in a time period of 10^8 years (as estimated from the $^{129}I/^{129}Xe$ chronometer). Rapidly evolving stars provided a "last minute" injection of fresh nucleosynthetic material, including ^{26}Al and ^{107}Pd, into the condensing cloud from which the Solar System was formed within a time period of a few million years.

Nucleocosmochronology

Nucleocosmochronology is the use of the relative abundances of radioactive nuclides to determine the time scales for nucleosynthesis of these nuclides. Schramm & Wasserburg (1970) showed that a nucleosynthetic formalism can be developed for long-lived radionuclides, and that this can give the mean age of the elements, independent of the time-dependent production model adopted. This mean age is a lower limit to the period T over which nucleosynthesis has taken place.

The estimate of the duration of nucleosynthesis is a challenging scientific problem. If we can calculate this period T, then we can estimate the age of the galaxy T_G by adding T to the age of the Solar System T_{ss} and the formation age of the Solar System Δ, such that

$$T_G = T + \Delta + T_{ss.}$$

This estimate is then a lower limit for the age of the universe.

I have already mentioned the work on the $^{176}Lu/^{176}Hf$ cosmochronometer by Malcolm McCulloch, Kevin Rosman and myself in the mid-1970s, (McCulloch *et al.* 1976). I was anxious to calibrate this chronometer because I thought it offered the best chance of measuring the duration of nucleosynthesis and hence the age of the Universe.

Although the $^{176}Lu/^{176}Hf$ ratio was known from mass spectrometric determinations in our laboratory, and the neutron capture values and half life of ^{176}Lu had been measured, the nuclear systematics of ^{176}Lu were not well understood in the mid 1970's. When ^{176}Lu is formed by the capture of ^{175}Lu by a neutron, it can exist in two isomeric states - the ground state which decays to ^{176}Hf with a half life of 3.57×10^{10}a, and an excited state which has a half life of only 3.68 hours (Figure 8).

In the mid 1970's it was believed that the two states were completely independent and thus all that was required was to measure the branching ratio B, that is find out what fraction of ^{176}Lu existed in the ground state. I persuaded some nuclear physicists at Lucas Heights Atomic Energy Establishment in NSW to help me to measure the branching ratio in their nuclear accelerator, which could simulate the

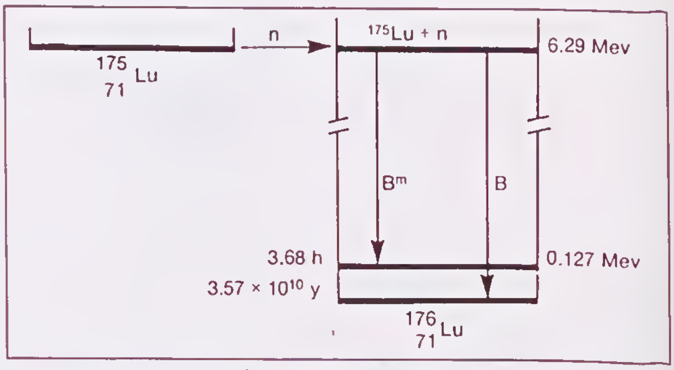

Figure 8. Decay scheme for neutron capture on ^{175}Lu, showing the two possible radioactive decay modes of ^{176}Lu to ^{176}Hf.

conditions that existed in red giant stars. We obtained a value of B = 21% (Allen *et al.* 1981). I remember, as if it was yesterday, making the calculations to estimate the age of nucleosynthesis from the data, and the shock of finding a negative age. This implied that the Big Bang had not yet occurred! There was obviously a small problem somewhere. So for the next 12 months or so, we laboriously repeated the branching ratio experiment, necessitating several trips to Lucas Heights. However, the value remained essentially unchanged. Furthermore our value was in conflict with a value of B from a much more prestigious group in Karlsruhe in Germany (Beer *et al.* 1984), so that we were understandably nervous about our conclusion, which was that the $^{176}Lu/^{176}Hf$ chronometer couldn't keep time.

The correct answer finally emerged when the energy levels of ^{176}Lu were remeasured. It turned out that the energy separation between the ground state and excited state of ^{176}Lu was much smaller than first reported in the literature, and at the temperatures which existed in red giant stars (10^8 K), the two states could overlap and hence the ^{176}Lu ground state could leak away via the ^{176}Lu excited state to ^{176}Hf. This problem is somewhat akin to the U-He leakage method. ^{176}Lu was a cosmothermometer not a cosmochronometer (De Laeter *et al.* 1988). Sufficient to say that this was a terribly disappointing result. I had spent almost ten years of research investigating the age of the Universe only to find that Nature had managed to frustrate us. The one pleasing fact that has emerged is that our conclusions have now been accepted by the international scientific community, including the Karlsruhe group (Lesko *et al.* 1991).

An independent estimate of the age of the Universe, calculated from the Hubble recession of the Galaxies, is approximately 19×10^9y (Sandage & Tamman 1982). Other astrophysical evidence on globular clusters, and estimates of the age of nucleosynthesis by the U-Pb (Thielemann *et al.* 1983) and Re-Os (Yokoi *et al.* 1983) cosmochronometers, give tentative support to this value, but it must be emphasised that the age is an approximate value with large uncertainties.

Thus cosmochronological studies have provided a reasonable time scale for the early history of the Solar System, including the age of formation of the meteorites. Some success has also been achieved in deriving a mean age of galactic nucleosynthesis, but the age of the galaxy has not yet been accurately determined from nucleocosmochronological studies due to the constraints associated with each of the long-lived chronometers used to determine the duration of nucleosynthesis.

Conclusions

I have endeavoured to give you a cursory glimpse of our endeavours to delve into that most intriguing Question of Time. As Arthur Holmes' has said:

> "It is perhaps a little indelicate to ask our Mother Earth her age, but Science acknowledges no shame, and from time to time has boldly attempted to wrest from her a secret which is proverbially well guarded".

My journey in time commenced in 1968 when Alec Trendall and Bill Compston came to visit me in the Mass Spectrometry Laboratory at WAIT 25 years ago, almost to the day, and persuaded me to assist in that indelicate question of asking Mother Earth her age.

Looking back down that 25 year time period (which is something I probably wouldn't have done if it was not for this Lecture) my over-riding impression is how much still remains to be achieved. Although we have developed beautiful "high-tech" mass spectrometers and many measurements have been made, some of the objectives we set out to achieve haven't been accomplished. But I look to the future with confidence. SHRIMP is a mass spectrometer which is ideally suited to unravelling the problems of mineral exploration, and we have an excellent team of physicists and geologists from UWA, GSWA, and Curtin together with overseas collaborators, who can exploit its potential to the full.

My most enduring memories of my chronological odyssey have been the people I have worked with, the friendships made, the teamwork forged, the localities visited. Maybe one day we will learn all the answers, but in the meantime perhaps we should listen to Tolly Cobbold's injunction "Time, Gentlemen, Time", and leave some of the questions to another time and perhaps to another Royal Society Medallist to answer.

Acknowledgements: The outstanding contribution of Dr Peter Jeffery in the establishment of geochronology in Australia, and the work of Prof Bill Cnmpston who has recently received an FRS for his development of SHRIMP and other initiatives, together with the long standing interest of Drs Alec Trendall, Will Libby, Ian Fletcher and others, needs to be recognised. I would like to acknowledge my family, research colleagues and students for their contribution and support to the work described in this review. I would also wish to thank Curtin University of Technology and the Australian Research Council for supporting the mass spectrometry laboratory over a period of twenty five years. Ms Tiffanie Carr prepared this manuscript with her usual skill and efficiency.

References

Aldrich L T & Nier A O 1948 Argon 40 in potassium minerals. Physical Review 74: 876-877.

Allen B J, Lowenthal G C & De Laeter J R 1981 S-process branch at ^{176}Lu. Journal of Physics G: Nuclear Physics 7: 1271-1284.

Aston F W 1929 The mass spectrum of uranium lead and the atomic weight of proactinium. Nature 123: 313.

Beer H, Walter G, Macklin R L & Patchett P J 1984 Neutron capture cross sections and solar abundances of ^{160,161}Dy, ^{170,171}Yb, ^{175,176}Lu and ^{176,177}Hf for the s-process analysis of the radionuclide ^{176}Lu. Physical Review C. 30: 464-478.

Bickle M J, Bettenay L F, Barley M E, Chapman H J, Groves D I, Campbell I H & De Laeter J R 1983 A 3500 Ma Plutonic and Volcanic Calc-Alkaline Province in the Archaean East Pilbara Block. Contributions of Mineralogy and Petrology 84: 25-35.

Chapman H J, Bickle M J, De Laeter J R, Bettenay L F, Groves D I, Andersen L S, Binns R A & Gorton M 1981 Rb-Sr geochronology of granitic rocks from the Diemals area, Central Yilgarn Block. Special Publication No. 7 Geological Society of Australia, 173-186.

Clarke W B, De Laeter J R, Schwarcz H P & Shane K J 1970 ^{26}Al/^{26}Mg dating of feldspar in meteorites. Journal of Geophysical Research 75: 448-462.

Compston W, De Laeter J R & Vernon M J 1972 Strontium isotope geochemistry of Apollo 15 basalts. In: The Apollo 15 Lunar Samples. (Chamberlain, J.W. & Watkins) The Lunar Science Institute, 347-351.

Compston W & Jeffery P M 1959 Anomalous "common strontium" in granite. Nature, 184: 1792-1793.

Compston W & Pidgeon R T 1986 Jack Hills, evidence of more very old detrital zircons in Western Australia. Nature 321: 766-769.

Cotton L A 1926 Age of certain radium-bearing rocks in Australia. American Journal of Sciences 12: 42-45.

De Laeter J R, Allen B J, Lowenthal G C & Boldeman J W 1988 Constraints on the ^{176}Lu cosmochronometer. Journal of Astrophysics and Astronomy 9: 7-15.

De Laeter J R, Fletcher I R, Rosman K J R, Williams I R, Gee, R D & Libby W G 1981 Early Archaean gneisses from the Yilgarn Block, Western Australia. Nature 292: 322-324.

De Laeter J R, Fletcher I R, Bickle M J, Myers J S, Libby W G & Williams I R 1985 Rb-Sr, Sm-Nd, Pb-Pb geochronology of ancient gneisses from Mt Narryer, Western Australia. Australian Journal of Earth Sciences 32: 349-358.

De Laeter J R & Libby W G 1993 Early Palaeozoic biotite Rb-Sr dates in the Yilgarn Block, near Harvey, Western Australia. Australian Journal of Earth Sciences 40: 445-453.

De Laeter J R, Libby W G & Trendall A F 1981 The Older Precambrian Geochronology of Western Australia. Special Publication of the Geological Society of Australia 7: 145-157.

De Laeter J R & Rosman K J 1984 A pnssible ^{126}Sn chronometer for the early solar system. Meteoritics 19: 217.

De Laeter J R & Trendall A F 1970 The age of the Copper Hills porphyry. Western Australia Geological Survey Annual Report 1969: 54-59.

De Laeter J R & Trendall A F 1979 The contribution of geochronology to precambrian studies in Western Australia. Journal of the Royal Society of Western Australia 62: 21-31.

De Laeter J R, Vernon M J & Compston W 1973 Revision of lunar Rb-Sr ages. Geochimica et Cosmochimica Acta 27: 700-702.

Fletcher I F & Rosman K J R 1980 The effect of trace gases on neodymium ion formation. International Journal of Mass Spectrometry and Ion Physics 36: 253-257.

Froude D O, treland T R, Kinny P D, Williams I S, Compston W, Williams I R. & Myers J S 1983 Ion Microprobe identification of 4100 to 4200 Ma-old terrestrial zircons. Nature 304: 616-618.

Gee R D, Baxter J L, Wilde S A & Williams I R 1981 Crustal development in the Archaean Yilgarn Block, Western Australia. Geological Society of Australia, Special Publication 7: 43-56.

Gray C & Compston W 1974 Excess ^{26}Mg in the Allende meteorite. Nature 251: 495-497.

Greenhalgh D & Jeffery P M 1959 A contribution to the Precambrian chronology of Australia. Geochimica et Cosmochimica Acta 16: 39-57.

Holmes A & Lawson R W 1927 Factors involved in the calculation of the ages of radioactive minerals. American Journal of Science 13: 327-344.

Holmes A 1927 The age of the Earth. Benn's Six penny Library No 102, London, Ernest Benn Ltd.

Jeffery P M 1976 Stable Isotope Abundance Studies in Western Australia. Australian Physicist 13: 26-28.

Jeffery P M, Compston W, Greenhalgh D & De Laeter J R 1955 On the Carbon-13 Abundance of Limestones and Coals. Geochimica et Cosmochimica Acta 7: 255-286.

Jeffery P M & Reynolds J H 1961. Origin of the excess ^{129}Xe in stone meteorites. Journal of Geophysical Research 66: 3582-3584.

Jenkin J G 1985 Frederick Soddy's 1904 Visit to Australia and the Subsequent Soddy-Bragg Correspondence: Isolation from Without and Within. Historical Records of Australian Science 6: 153-169.

Kelly W R & Wasserburg G J 1978 Evidence for the existence of ^{107}Pd in the early solar system. Geophysical Research Letters 5: 1079-1082.

Kinny P D, Williams I S, Froude D O, Ireland T R & Compston W 1988 Early Archaean zircon ages from orthogneisses and anorthosites at Mount Narryer, Western Australia. Precambrian Research 38: 328-341.

Kober B, Pidgeon R T & Lippolt H J 1989 Single-zircon dating by stepwise Pb - evaporation constrains the Archaean history of detrital zircons from The Jack Hills, Western Australia. Earth and Planetary Science Letters 91: 286-296.

Lee T, Papanastassiou D A & Wasserburg G J 1977 Aluminium-26 in the early solar system : fossil or fuel? Astrophysical Journal Letters 211: L107-L110.

Lesko K T, Norman E B, Larimer R M, Sur B & Beausang C B 1991 ^{176}Lu : An unreliable s-process chronometer. Physical Review C 44: 2850-2864.

McCulloch M T, De Laeter J R & Rosman K J R 1976 The isotopic composition and elemental abundance of lutetium in meteorites and terrestrial samples and the ^{176}Lu cosmochronometer. Earth and Planetary Sciences Letters 28: 308-322.

McCulloch M T & Wasserburg G J 1978a Sm-Nd and Rb-Sr chronology of continental crust formation. Science 200: 1003-1011.

McCulloch M T & Wasserburg G J 1978b Barium and neodymium isotopic anomalies in the Allende meteorite. Astrophysical Journal 220: L15-L19.

Nier A O 1940 A mass spectrometer for routine isotope abundance measurements. Review of Scientific Instruments 11: 212-216.

Nier A O, Thompson R W & Murphey B F 1941 The isotopic constitution of lead and the measurement of geological time. Physical Review 66: 112-116.

Patterson C C 1956 Age of meteorites and the earth. Geochimica et Cosmochimica Acta 10: 230-237.

Reynolds J H 1960 Determination of the age of the elements. Physical Review Letters 4: 8-10.

Rutherford E 1906 Radioactive Transformations. Yale University Press, New Haven.

Rutherford E 1929 Origin of actinium and the age of the earth. Nature 123: 313-314.

Sandage A & Tammann G A 1982 Steps towards the Hubble constant with the global value. Astrophysical Journal 256: 339-345.

Schramm D N & Wasserburg G J 1970 Nucleochronologies and the mean age of the elements. Astrophysical Journal 162: 57-69.

Simpson E S 1910 Pilbarite, a new mineral from the Pilbara Goldfields : Verbatim report of paper read to National History and Science Society of Western Australia. West Australian, 17 August 1910.

Tera F, Papanastassiou D A & Wasserburg G J 1974 Isotopic evidence for a terminal lunar cataclysm. Earth and Planetary Sciences Letters 22: 1-21.

Thielemann F K, Metzinger J & Klapdor H V 1983 Beta delayed fission and neutron emission: Consequences for the astrophysical r-process and the age of the galaxy. Zeitschrift fur Physik A 309: 301-317.

Wasserburg G J 1987 Isotopic abundances: Inferences on solar system and planetary evolution. Earth and Planetary Sciences Letters 86: 129-173.

Wasserburg G J, Papanastassiou D A, Tera F & Huneke J C 1977 The accumulation and bulk composition of the Moon. Philosophical Transactions of the Royal Society, London A 285: 7-22.

Wilson A F, Compston W, Jeffery P M & Riley G H 1960 Radioactive Ages from the Precambrian rocks in Australia. Journal of the Geological Society of Australia 6: 179-196.

Yokoi K, Takahashi K & Arnould M 1983 The ^{187}Re-^{187}Os chronology and chemical evolution of the galaxy. Astronomy and Astrophysics 117: 65-82.